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SCIENTIFIC TRANSLATION SERVICES
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(19) Patent Office of Japan (JP)

(12) Patent Disclosure Bulletin (A)

(11) Patent Disclosure No.: Sho 62-[1987]-81,416

(51) Int. Cl. ⁴ :	Identification Code:	Interagency Reference No.:
C 08 G 59/62	N J S	A-6561-4J
59/50	N J E	C-6561-4J
	1 0 1	
59/62	N J L	B-6561-4J
H 01 L 23/30		R-6835-5F

(43) Disclosure Date: April 14, 1987

Request for Examination: not requested No. of Inventions: 1 (Total 6 pages)

(54) Title of the Invention: **EPOXY RESIN COMPOSITIONS FOR SEALING A SEMICONDUCTOR**

(21) Application No.: Sho 60-[1985]-220,258

(22) Application Date: October 4, 1985

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SPECIFICATION

1. Title of the Invention

EPOXY RESIN COMPOSITIONS FOR SEALING A SEMICONDUCTOR.

2. Scope of the Patent Claim

Epoxy resin compositions for sealing a semiconductor containing the following four necessary components:

- (1) an epoxy resin
- (2) a phenol type curing agent
- (3) a curing promoting agent consisting of (a) 1,8-diazabicyclo(5.4.0)-7-undecene and/or a salt derived from 1,8-diazabicyclo(5.4.0)-7-undecene and (b) a triorganophosphine with a weight ratio in the range of a:b = 90:10-5:95
- (4) 150-600 weight parts of an inorganic filler per 100 weight parts of the sum of (1) and (2) mentioned above.

3. Detailed Description of the Invention

(Field of Industrial Application)

The present invention pertains to an epoxy resin composition for sealing a semiconductor or especially for sealing LSI, etc., that increasingly require more thinness and more miniaturization than before in spite of the marked increase in the degree of integration in recent years.

(Prior Art)

Transfer molding using an epoxy resin composition is used most widely in recent years for sealing semiconductors, IC, LSI, etc., because such products require low cost, mass production and balanced reliability. However, with an increase in the degree of integration of semiconductors, demand for miniaturization of an instrument that uses semiconductors is also becoming stronger. Therefore, for the package of a semiconductor, especially LSI, etc., the use of a small and thin surface-mounted type package such as the conventional DIP type, a flat package, PLCC (Plastic Leadiess Chip Carrier) etc. is increasing.

Subsequently, various problems associated with the reliability not encountered in the past, especially the reliability in terms of moisture resistance, are appearing.

In the evaluation of the moisture resistance reliability of a resin for sealing a semiconductor in the past, the pressure cooker test (abbreviated below as PCT) in which evaluation elements etc. are transfer-molded with the test resin and then placed in saturated and pressurized water vapor or the bias pressure cooker test (abbreviated below as BPCT) in which the molded product is subject to bias is performed.

However, it is becoming clear that, in the case of the surface-mounted IC, LSI etc., the moisture resistance reliability at the time of mounting is reduced and evaluation using the said PCT or BPCT alone is no longer sufficient.

The solder reflow technique using infrared rays, the solder spraying technique (vapor phase soldering) and the vapor phase soldering technique utilizing a high-boiling-point solvent vapor are used in the mounting on the base board of the surface-mounted package. In all of these techniques, the entire package will be heated rapidly to the melting temperature of the solder of 200-300°C. Such a tremendous thermal impact can cause the problems mentioned above.

For the evaluation of a sealing resin for surface mounting, therefore, it is becoming routine to carry out PCT or BPCT after the molded product has been subject to a flux treatment and immersed in a soldering bath at 260°C for 10 seconds.

However, it has been shown that, among the materials used to blend the epoxy resin composition mentioned above, the curing promoting agent can greatly affect the moisture resistance reliability. It has been stated that, among curing promoting agents used in the past, 1,8-diazabicyclo(5.4.0)-7-undecene or its carboxylic

acid salts described in Patent Disclosure No. Sho 55-[1980]-5,929 and Patent Disclosure No. Sho 59-[1984]-94,761 and triorganophosphines described in Patent Publication No. Sho 57-[1982]-60,779 and Patent Publication No. Sho 59-[1984]-33,125 would yield especially good results.

(Problem to be Solved by the Invention)

However, even with the use of the said curing promoting agents, the satisfactory test results could not be obtained simultaneously from the conventional PCT or BPCT and the post-solder immersion PCT or BPCT. In other words, when 1,8-diazabicyclo(5.4.0)-7-undecene or its carboxylic acid salts are used, the test results especially from the conventional PCT are poor, whereas when triorganophosphine is used, the test results especially from the post-solder immersion PCT or BPCT are poor.

The present invention was developed in order to overcome the problem mentioned above. We found that especially when the curing promoting agent consisting of (a) 1,8-diazabicyclo(5.4.0)-7-undecene and/or a salt derived from 1,8-diazabicyclo(5.4.0)-7-undecene and (b) triorganophosphine in a weight ratio in the range of a:b = 90:10-5:95 is used, the test results not only from the conventional PCT or BPCT but also from the post-solder immersion PCT or BPCT could be improved markedly. These findings led us to develop the present invention. Namely, the present invention can provide an epoxy resin composition for semiconductor sealing that can yield excellent results not only in the conventional PCT or BPCT but also in the post-solder immersion PCT or BPCT.

(Means for Solving the Problem)

Namely, the present invention pertains to an epoxy resin composition for sealing a semiconductor that contains the following four necessary components:

- (1) an epoxy resin
- (2) a phenol type curing agent
- (3) a curing promoting agent consisting of (a) 1,8-diazabicyclo(5.4.0)-7-undecene (abbreviated below as DBU) and/or a salt derived from 1,8-diazabicyclo(5.4.0)-7-undecene (abbreviated below as a salt of DBU) and (b) a triorganophosphine with a weight ratio in the range of a:b = 90:10-5:95
- (4) 150-600 weight parts of an inorganic filler per 100 weight parts of the sum of (1) and (2) mentioned above.

The epoxy resins that can be used in the present invention can be any epoxy resins as long as they contain more than two epoxy groups per one molecule of resin. For example, bisphenol A type epoxy resins, novolak type epoxy resins synthesized from various phenols, glycidyl ester type epoxy resins, glycidyl amine type epoxy resins, straight-chain aliphatic epoxy resins, alicyclic epoxy resins, heterocyclic epoxy resins and these epoxy resins into which halogens such as chlorine, bromine, etc., have been incorporated can be used. One kind or more than two kinds of these epoxy resins may be used. Among these epoxy resins, novolak type epoxy resins are especially desirable. The smaller the contents of ionic impurities and the components that can be easily degraded to produce ions in the said epoxy resins, the better. More specifically, it is desirable that the contents of free sodium ions and chlorine ion should both be less than 5 ppm and those of hydrolyzable halogens should be less than 500 ppm.

The phenol type curing agents that can be used in the present invention should contain more than two phenolic hydroxide groups per one molecule of the curing agent. For example, such phenol type curing agents as novolak resins synthesized with the use of phenol, resorcinol, cresol, xlenol, propyl phenol, amyl phenol, butyl phenol, octyl phenol, phenyl phenol, allyl phenol, bisphenol A, etc., individually or concomitantly, polyisopropenyl phenols, polyvinyl phenols and such phenols to which halogen groups have been incorporated can be used. One kind or more than two kinds of these compounds can be used. Among these compounds, the novolak resins containing less than 1 wt. % of uncondensed phenolic compounds are desirable.

As for the blending quantity of the curing agent, it is desirable that the ratio of the phenolic hydroxyl group of the curing agent and the epoxy group of the epoxy resin is in the range of 0.5-1.5 or more preferably 0.7-1.2. A ratio outside of said range is not desirable because the moisture resistance reliability will be reduced.

As for the curing promoting agents (a) used in the present invention, e.g., DBU itself, such salts of DBU as, e.g., such organic carboxylic acid salts as DBU octylate, DBU oleate, DBU formate, DBU acetate, DBU benzoate, DBU phthalate, DBU trimellitate (or anhydride), DBU trimesate, etc., such salts of phenolic hydroxyl

group-containing compounds as DBU phenolate, DBU phenol novolak salts, DBU polyvinyl phenolate, etc., and DBU *p*-toluene sulfonate can be used.

As for the (b) that must be used together with (a), e.g., tributyl phosphine, trioctyl phosphine, tricyclohexyl phosphine, tribenzyl phosphine, triphenyl phosphine, tri-*p*-tolyl phosphine, bis-diphenyl phosphinoethane, bis-diphenyl phosphinobutane, etc., can be used. However, triphenyl phosphine, tri-*p*-tolyl phosphine, bis-diphenyl phosphinoethane, etc., in which aromatic groups are bonded directly to the phosphorus atom, are preferable.

The said (a) and (b) are used together and their weight ratio used has to be in the range of a:b = 90:10-5:95. When the ratio is outside of this range, the moisture resistance reliability, especially the moisture resistance reliability observed after immersion in a solder will become poor and the synergistic effect of the two components could not be realized.

The amount of the curing promoting agent added should be in the range of 0.05-5 weight parts or preferably 0.5-3 weight parts per 100 weight parts of the sum of (1) and (2) mentioned above. When the amount used is less than 0.05 weight part, the promoting effect could not be obtained, whereas when the amount used is greater than 5 weight parts, the formability and moisture resistance will be reduced.

The inorganic fillers that can be used in the present invention include, e.g., powders of crystalline silica, molten silica, talc, alumina, calcium sulfate, calcium carbonate, barium carbonate and glass fibers. They can be used individually or in a combination of two or more. Among these compounds, silica, especially molten silica are desirable because of their high purity and low coefficient of thermal expansion. As for the form that can be used, in addition to the ordinary powder form, spherical products may also be used.

The amount of the fillers used should be in the range of 150-600 weight parts per 100 weight parts of the sum of (1) and (2) mentioned above. The greater the amount used, the better, as long as the formability is not adversely affected.

If necessary, the following materials may be added and blended in an appropriate quantity into the epoxy resin compositions of the present invention: such mold releasing agents as carnauba wax, montan wax, higher fatty acids and their calcium salts, fluorine compounds, silicone oils, etc., such flame-retarding agents as halogenated epoxy resins and antimony trioxide, such coloring agents as carbon black, such surface treatment agents as silane coupling agents, etc.

In order to reduce the stress to the material to be sealed, such flexibility providing agents as silicone type rubber, butadiene type rubber, etc., may be blended into the epoxy resin compositions of the present invention without producing adverse effects. In fact, blending of such an agent may be beneficial to the achievement of the object of the present invention.

The epoxy resin compositions of the present invention can be prepared easily as described below. The required materials in a specified proportion are thoroughly mixed with the use of, e.g., a mixer. The mixture is then subject to a melting mixing treatment with the use of a roller or a kneader.

(Actual Examples)

The present invention will be explained in detail below with the use of actual examples.

Actual Examples 1-10 and Comparison Examples 1-7

Cresol novolak type epoxy resin with an epoxy equivalence of 210 (epoxy resin A), brominated phenol novolak type epoxy resin with an epoxy equivalence of 270 (epoxy resin B), phenol novolak resin (curing agent), DBU (curing promoting agent a_1), DBU octylate (curing promoting agent a_2), DBU phenol novolak resin salt (curing promoting agent a_3), triphenyl phosphine (curing promoting agent b), undecyl imidazole, molten silica powder (filler), carnauba wax, γ -glycidoxypentyltrimethoxy silane (silane coupling agent), carbon black and antimony trioxide in the proportions shown in the table were blended and mixed with the use of a mixer. The

mixture was then kneaded with the use of a heated roller, cooled and pulverized to obtain an epoxy resin composition.

In order to evaluate the moisture resistance reliability of the epoxy resin compositions thus obtained, a silicon element for evaluation having opposing aluminum wirings was subject to a transfer molding process using each of the compositions prepared above to obtain an 80-pin flat package. Some of the molded products as such were subject to PCT and BPCT. In PCT, the molded product was allowed to stand in saturated and pressurized water vapor at 125°C. In BPCT, a direct current voltage of 20 V was applied to the opposing aluminum wirings. The remaining molded products were immersed in a solder for 10 seconds and then subject to PCT and BPCT as described above. The time needed to cause poor opening in 50% of the elements tested was measured. The results of the evaluation are shown in the table.

Table

Blend ing com- posi- tion	Actual Example										Comparison Example						
	1	2	3	4	5	6	7	8	9	10	1	2	3	4	5	6	7
Epoxy resin A	90	90	90	90	90	90	90	90	90	90	90	90	90	90	90	90	90
Epoxy resin B	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Curing agent	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45
Curing promoting agent a ₁	0.07	0.2	0.45	0.75	1.1	1.25	-	-	-	-	-	0.03	1.35	1.5	-	-	-
Curing promoting agent a ₂	-	-	-	-	-	-	0.7	-	0.7	0.7	-	-	-	-	1.8	-	-
Curing promoting agent a ₃	-	-	-	-	-	-	-	0.6	-	-	-	-	-	-	-	1.4	-
Curing promoting agent b	0.95	0.85	0.7	0.5	0.27	0.2	0.7	0.6	0.7	0.7	1	0.98	0.1	-	-	-	-
Unidexyl imidazole	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.5
Filler	350	350	350	350	350	350	350	350	400	400	350	350	350	350	350	350	350
Carnauba wax	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
Silane coupling agent	4	4	4	4	4	4	4	4	5	6	4	4	4	4	4	4	4
Carbon black	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Antimony trioxide	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Ratio of curing promoting agents a/b	7/93	19/81	39/61	60/40	80/20	86/14	50/50	50/50	50/50	50/50	0/100	3/97	93/7	100/0	100/0	100/0	-
PCT (hours)	> 2000	> 2000	> 2000	> 2000	> 2000	> 2000	> 2000	> 2000	> 2000	> 2000	1500	1500	> 2000	> 2000	> 2000	> 2000	800
BPCT (hours)	360	380	380	380	340	320	340	360	420	460	340	340	200	180	160	180	100
After Immersion in a solvent	650	800	850	900	700	650	850	800	1000	1000	300	300	500	500	450	500	200
BPCT (hours)	220	260	280	280	260	240	300	280	360	440	120	120	180	160	160	180	60

The actual examples described above indicate that when (a) alone was used as the curing promoting agent, the results of the conventional BPCT were poor. When (b) alone was used, the results of PCT and BPCT performed after the immersion in a solder were poor. In contrast, when the epoxy resin composition of the present invention was used, the results of PCT and BPCT were about the same and the results of PCT and BPCT performed after immersion in a solder were especially good, indicating that the epoxy resin composition of the present invention is suitable for use in the surface mounting type package such as the flat package or PLCC.

(Effect of the Invention)

As mentioned above, the epoxy resin composition for sealing a semiconductor of the present invention in which two kinds of curing promoting agent are blended in a specified proportion can yield excellent results in PCT and BPCT as well as the post-solder immersion PCT and BPCT.

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